Nanoparticle clusters:

An introduction to small-angle x-ray scattering (SAXS)

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CALIPSO SEMINAR 30TH NOV 2005

Collaborators

Goethite nanoparticles:

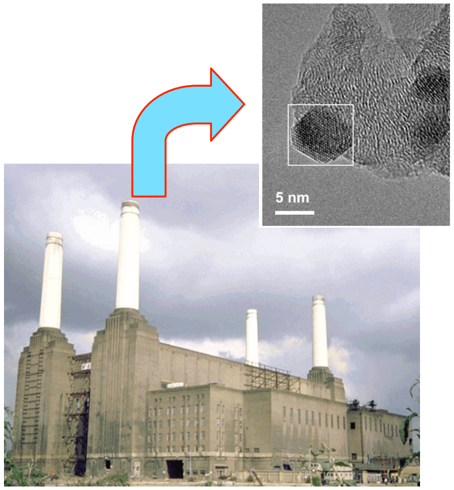
- Chris Kim Chapman University, CA
  - Nanogoethite synthesis and characterization
- Guopeng Lu LBNL
  - Lattice Boltzmann simulation
- Mike Toney SSRL
  - Simulated annealing

SSRL Scientific support:

- John Pople

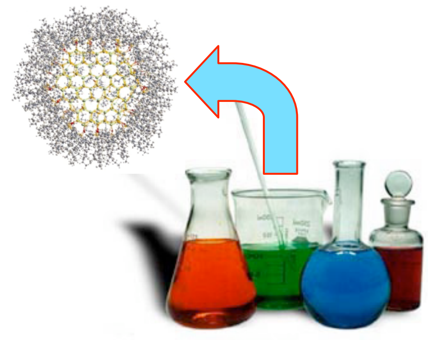
Funding - LBNL LDRD & DOE BES

Sources of Nanominerals



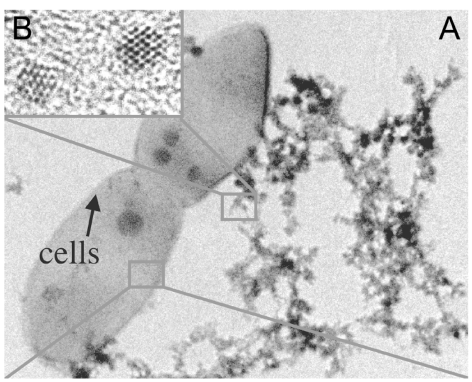
Combustion products

Man-made

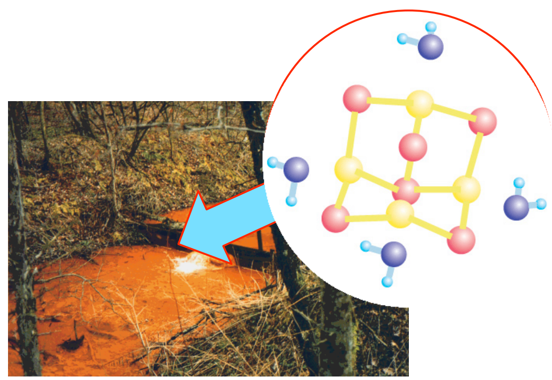


Chemical synthesis

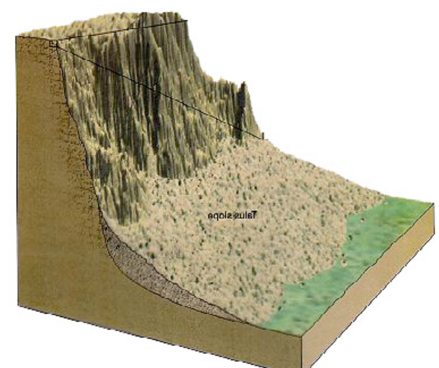
Natural



Biomineralization



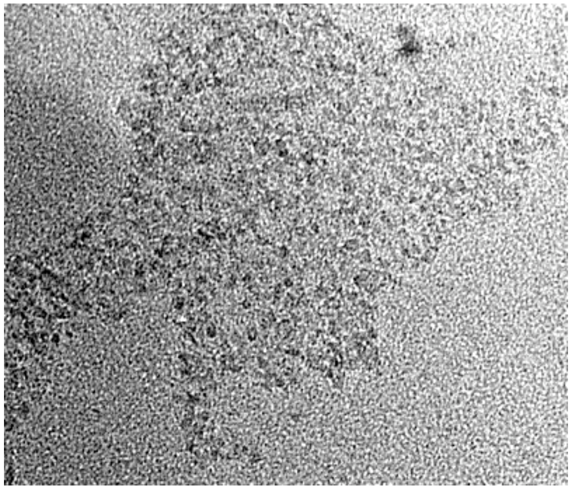
Inorganic precipitation



Weathering

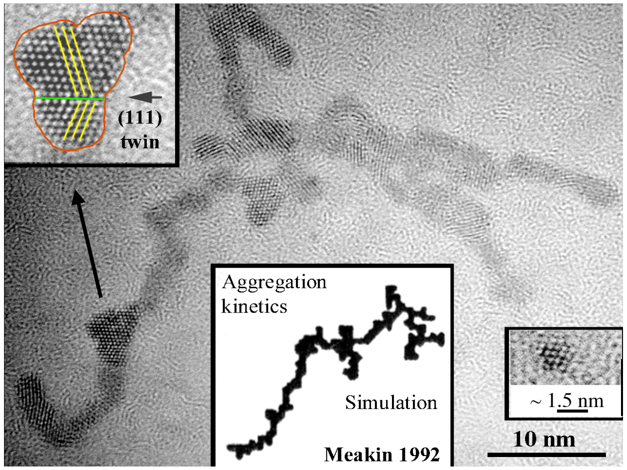
Nanoparticle Aggregation Morphologies

α-FeOOH nanoparticles



Chris Kim
unpublished

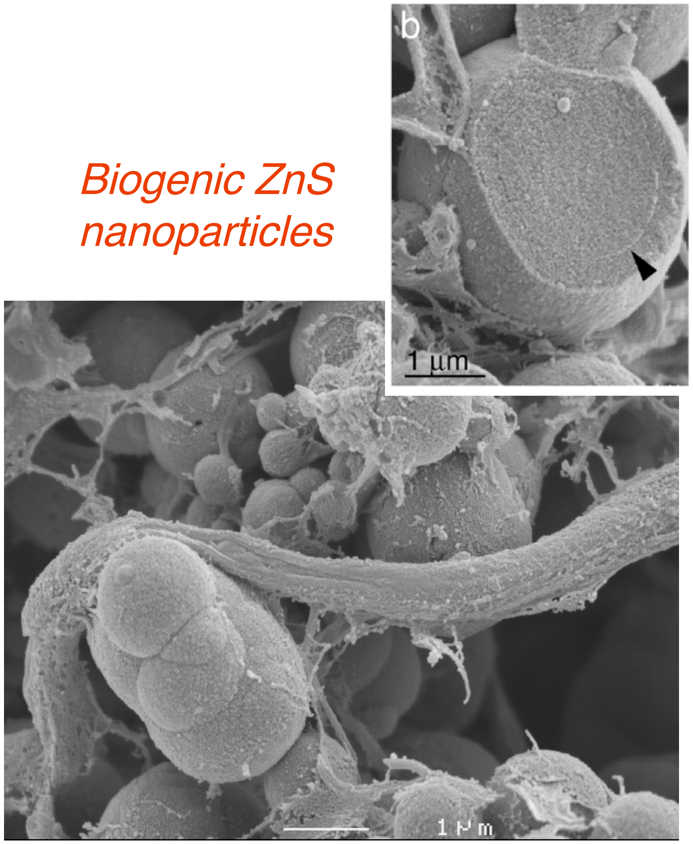
Biogenic UO_2 nanoparticles



Suzuki et al., *Nature* **419**, 134 (2002)

Moreau et al.,
Am. Mineral. **89**,
950 (2004)

Biogenic ZnS nanoparticles



Labrenz et al., *Science* **290**, 1744 (2000)

Consequences of Aggregation

- Mineral Growth
  - Aggregation-based pathways
- Transport
  - Bioremedation efficacy
- Surface Geochemical Processes
  - Ligand-mediated dissolution
- Detection
  - Induced polarization methods

Nanoparticles in Aqueous Environments

1 • Under what conditions do nanoparticles aggregate?

- Size, solution chemistry *experiment*
- Derive interparticle forces *modeling*

2 • What aggregate structures are formed?

- Measure cluster size, morphology, density *experiment*
- Simulate aggregation processes *modeling*

3 • How do aggregates travel through porous media?

- Flow column experiments *experiment*
- Simulate settling and straining effects *modeling*

Nanoparticles in Aqueous Environments

1 • Under what conditions do nanoparticle

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Small-angle x-ray scattering

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Small-angle X-ray Scattering

Suggested reading:

Neutron, X-ray and Light Scattering: Introduction to an Investigative Tool for Colloidal and Polymeric Systems

P. Lindner & Th. Zemb (Eds.)

North-Holland, Amsterdam, 1991

www.alibris.com
www.zubalbooks.com

X-ray scattering basics

$$q = \frac{4\pi}{\lambda}\sin\theta$$

$$\boxed{q = \frac{2\pi}{d}}$$

- SAXS: small-angle x-ray scattering

  10^{-3} Å^{-1} $< q_{max} <$ 0.1 Å^{-1}

  - Scattering from electron density contrast

- WAXS: wide-angle x-ray scattering

  $0 < q_{max} <$ 5 Å^{-1}

  - Equivalent to conventional X-ray Diffraction (XRD)

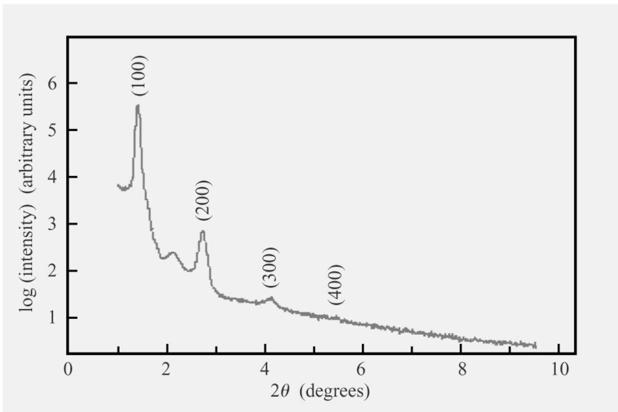
- High-energy WAXS:

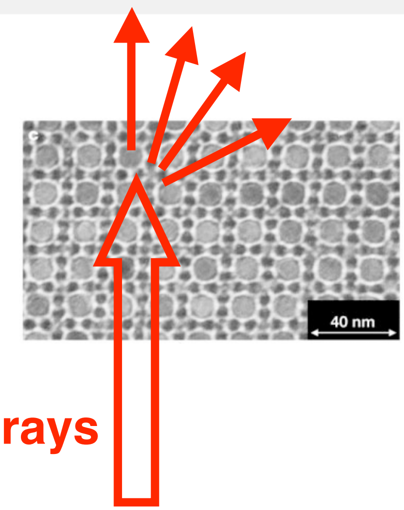
  $q_{max} >$ 20 Å^{-1}

  - Fourier inversion provides the real-space Pair Distribution Function

Small-angle X-ray Scattering

SAXS = diffraction from particles



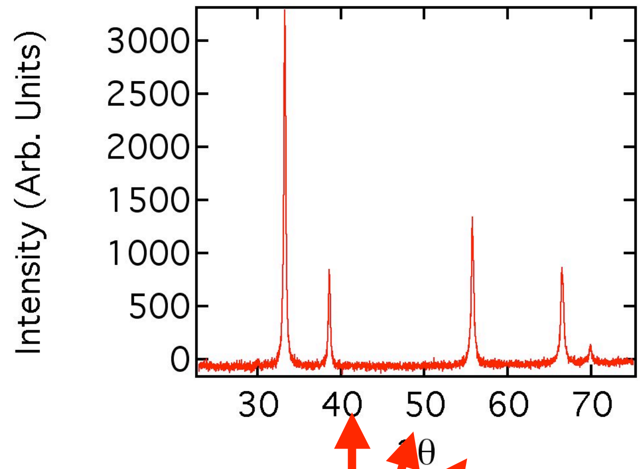


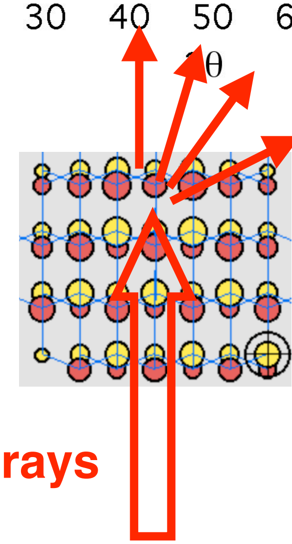
oriented Fe_2O_3
and PbS
nanoparticles

x-rays

Redl et al., *Nature* **423**, 968 (2003)

WAXS = XRD = diffraction from atoms



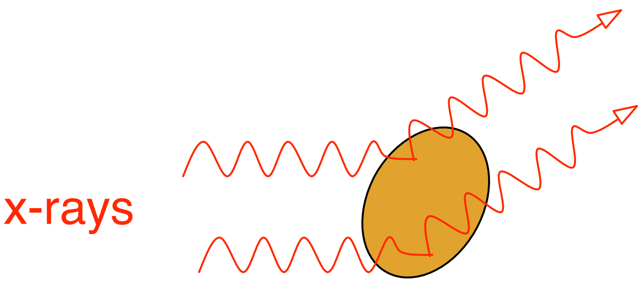


ZnS crystal

x-rays

Small-angle X-ray Scattering

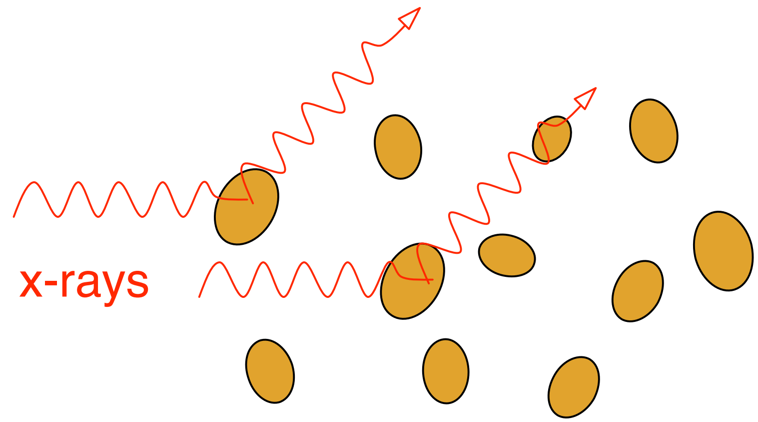
***P(q)* = particle scattering**



Dilute solutions:

$I(q) = P(q)$

***S(q)* = interparticle scattering**



Concentrated solutions or aggregates:

$I(q) = S(q)P(q)$

(identical particles)

Scattering vs. q, not θ :

$$q = \frac{4\pi}{\lambda}\sin\theta \qquad q = \frac{2\pi}{d}$$

Small-angle X-ray Scattering

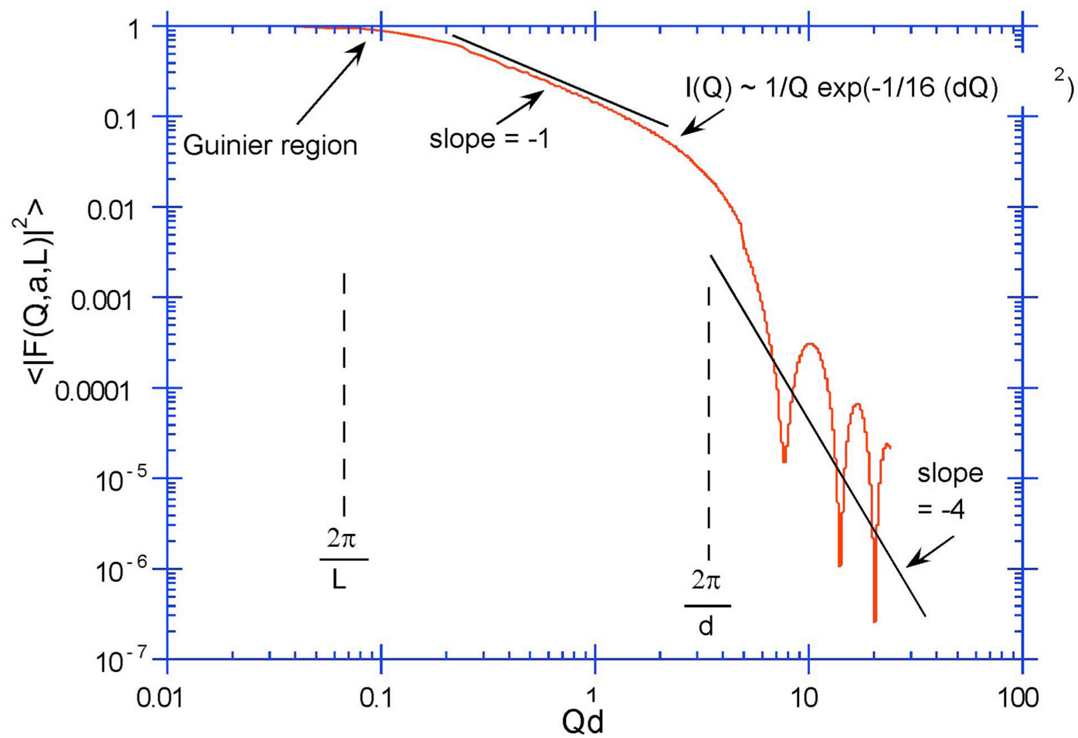
The particle scattering, *P(q)*, depends on the shape of the particle

$$P(q) = \int \Delta\rho^2 \frac{\sin(qr)}{qr} 4\pi r^2 dr$$

E.g., Form factor, *F(q)*, for rods length L = 80 nm, diameter d = 4 nm

Guinier region

$$I(q) = P(0)\exp\left[-\frac{q^2 R_g}{3}\right]$$



Small-angle X-ray Scattering

The Structure Factor, *S(q)*, given by relative arrangement of particles

***S(q)* is related to statistical descriptions of the particle positions:**

the particle-particle pair correlation functions, *g*(*r*)

Computationally convenient. *S(q)* can be calculated just like the Debye Eqn for x-ray diffraction

e.g., for *N* particles of known position

$$S(q) = 1 + \frac{1}{N} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{\sin(qr_{ij})}{qr_{ij}}$$

… this is a discrete sin-transform of *g*(*r*)!

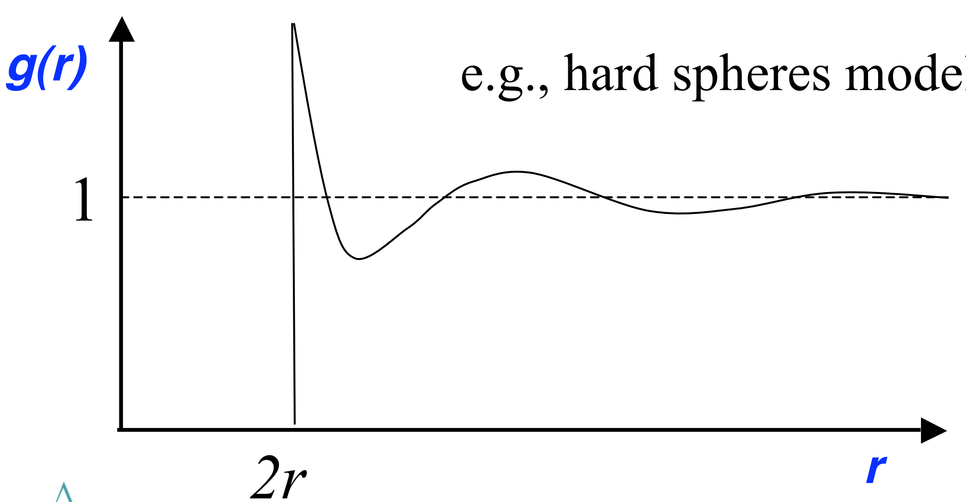
Small-angle X-ray Scattering

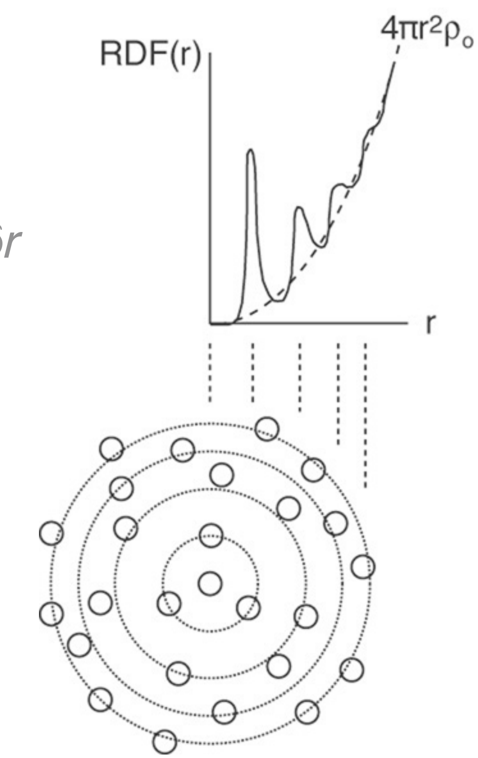
The Structure Factor, *S(q)*, given by FT of the pair correlation function, *g(r)*

$$S(q) = 1 + \frac{N}{V}\int 4\pi r^2\left[g(r) - 1\right]\frac{\sin(qr)}{qr}\,dr$$

Definition of *g(r)*

1D representation of **3D** structure
Related to the **radial distribution function** (RDF)
Probability of finding another particle within $r \rightarrow r + \delta r$





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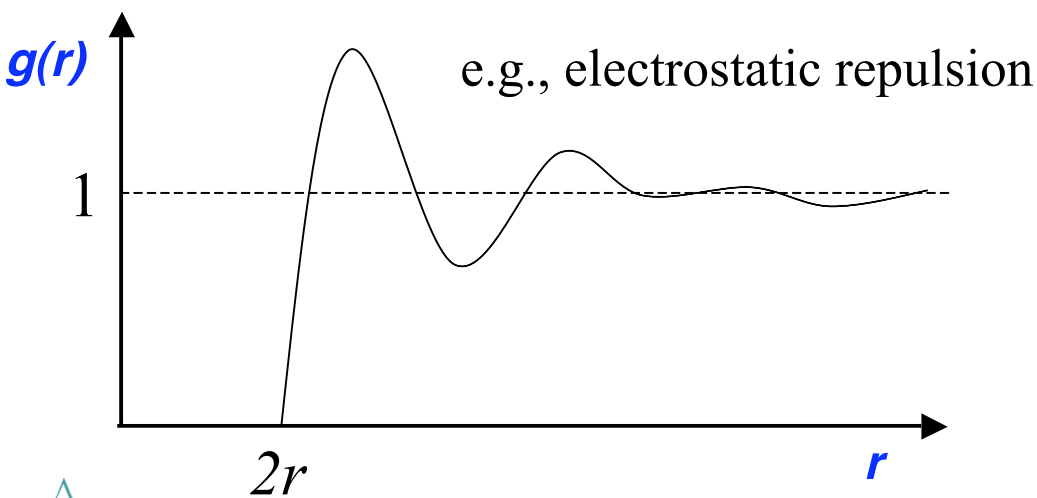

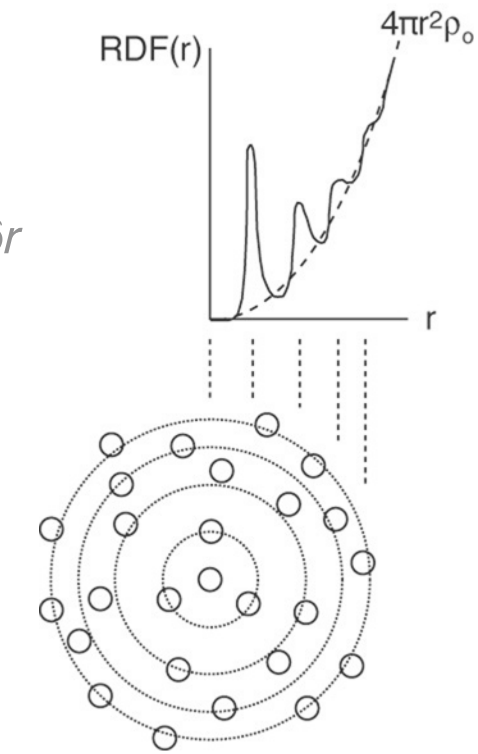

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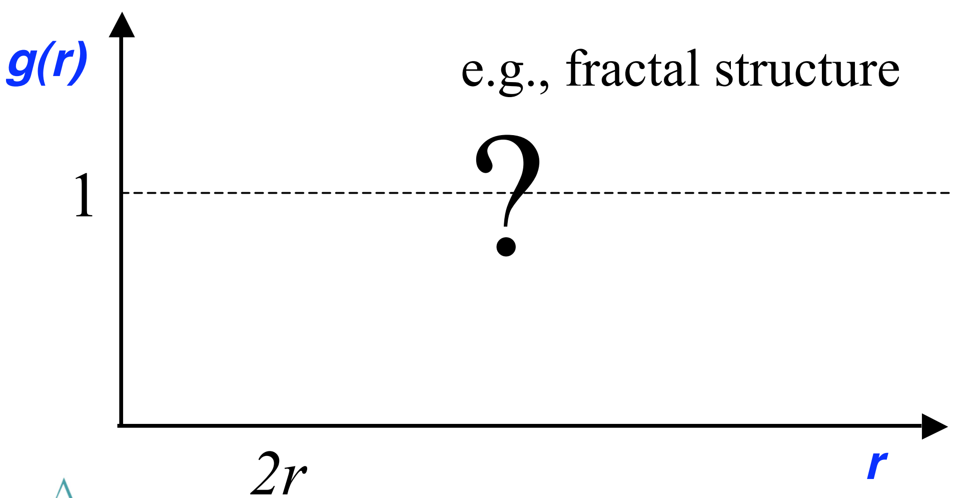
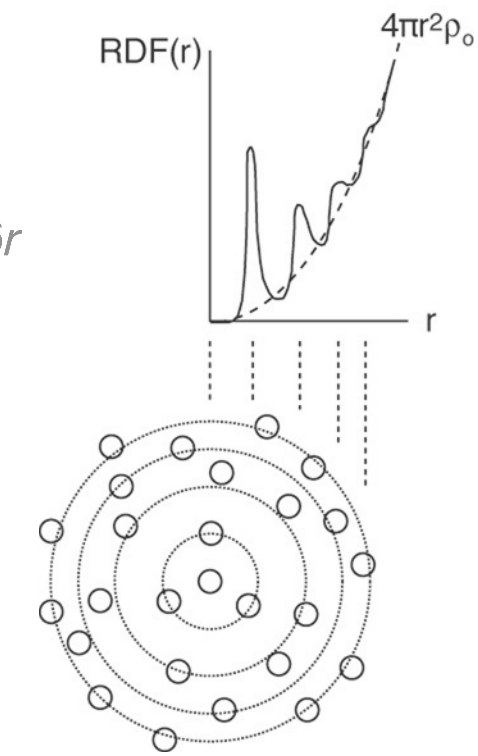




Small-angle X-ray Scattering

Analysis of SAXS data for aggregates = estimating *g(r)*

I. Analytical expression for *g(r)*

e.g. fractal aggregates

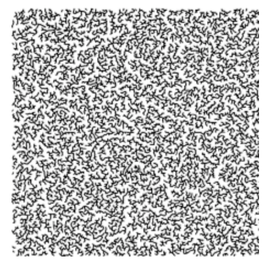
$$\left[g(r)-1\right] \propto r^{D_F - 3} \exp\left(-r/\xi\right)$$

e.g. hard spheres

Complex coupled equations

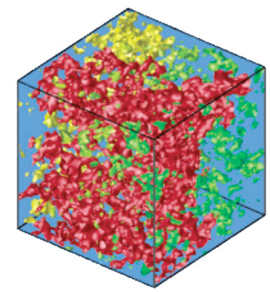
II. Simulate *g(r)*

constrain *n(r)*, *P(q)*



van Garderen et al., *J. Chem. Phys.* **102**, 480 (1995)

Computer model

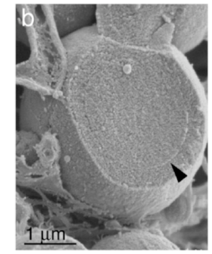


Hedstrom et al., *Langmuir* **20**, 1535 (2004)

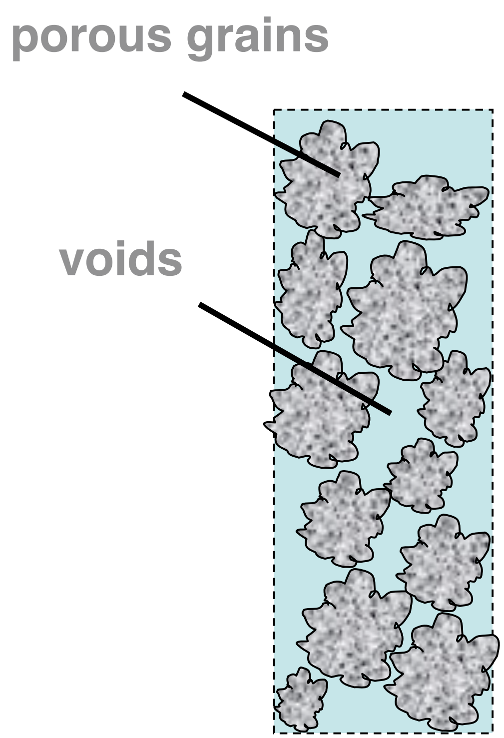
Simulated SAXS

Experimental SAXS

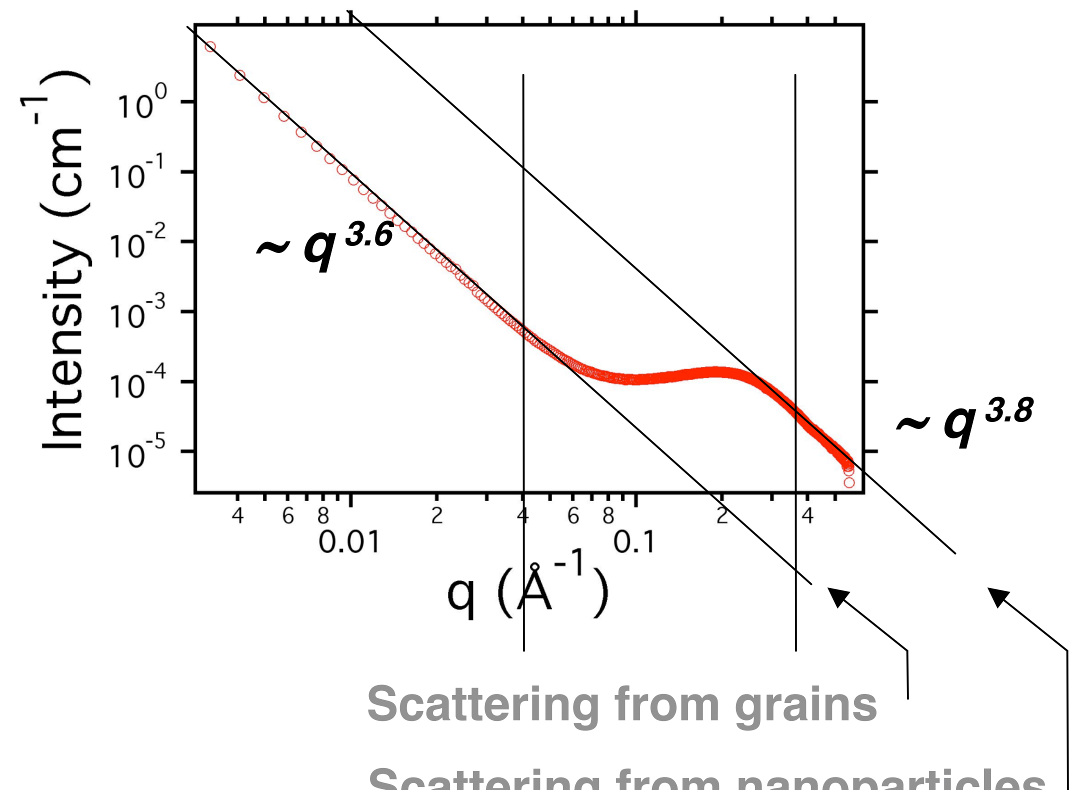
SAXS from Porous Media



Two length scales - *two Porod regions*



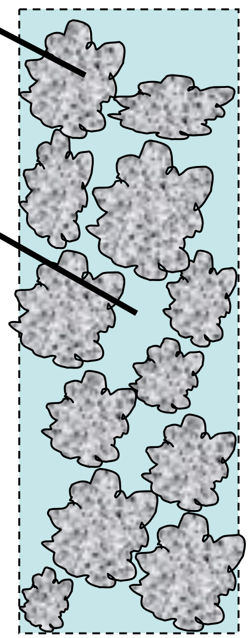
SAXS from dried ZnS nanoparticles



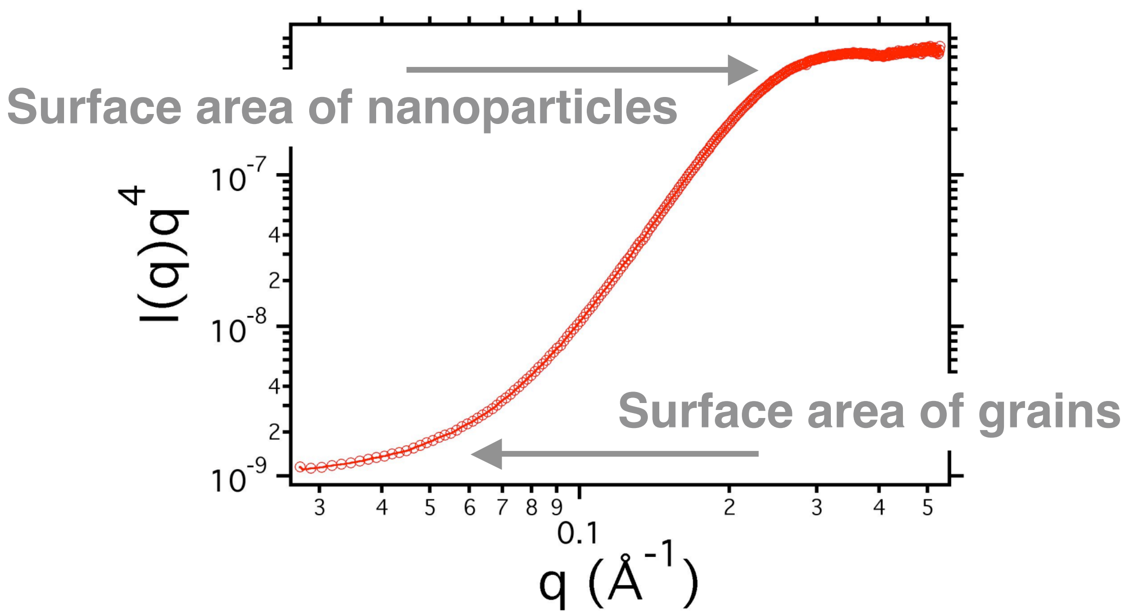
Theory: Spalla et al., *J. Appl. Cryst.* **36**, 338 (2003)

SAXS from Porous Media

Two length scales - *two Porod regions*



Asymptotes give two surface areas



Ratio of surface areas = 600

Theory: Spalla et al., *J. Appl. Cryst.* **36**, 338 (2003)

Colloid Behavior of Goethite Nanoparticles

Research plan:

SAXS of nanoparticle dispersions
interparticle interaction forces

Simulations of aggregation
real-space aggregate structure

SAXS of aggregates
test simulations

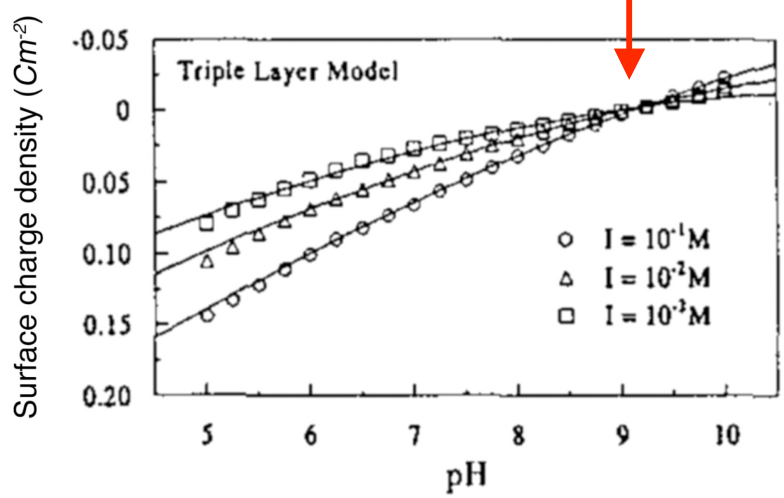
Calculation of hydrodynamic properties

Larger scale transport experiments

Colloid Behavior of Goethite Nanoparticles

Surface charge vs. pH

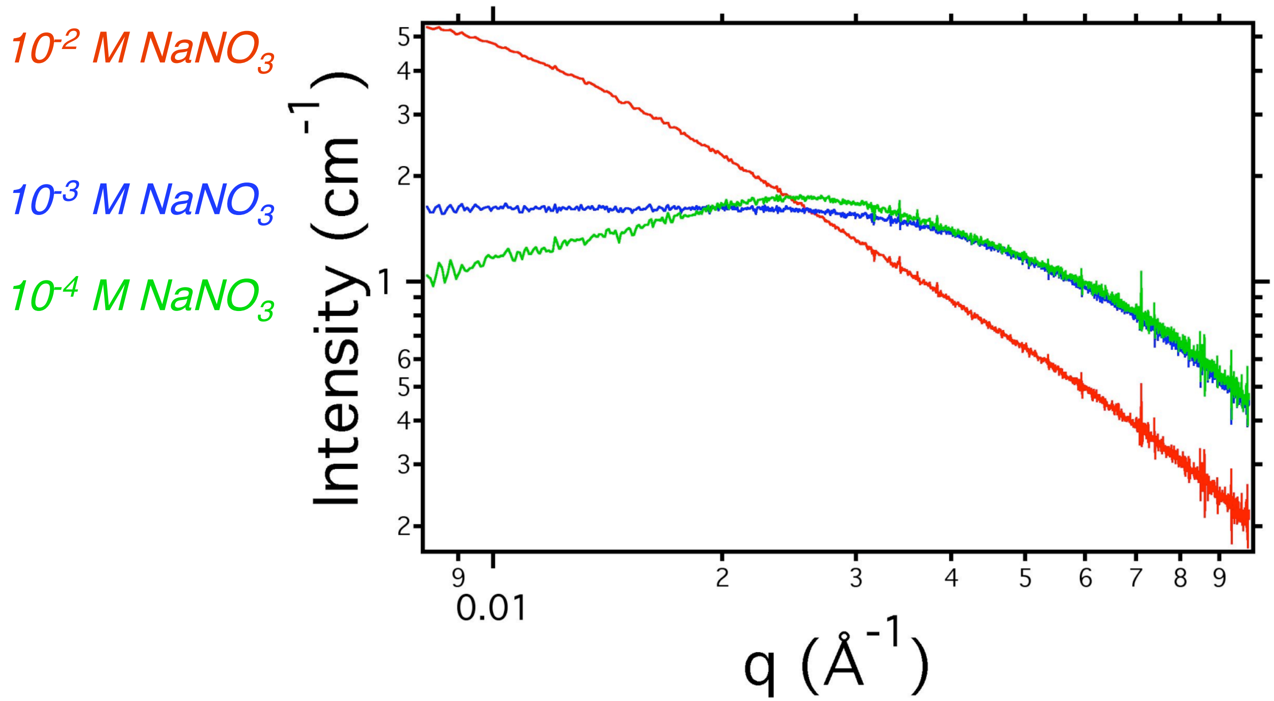
$pH_{ZPC} \approx 9.1$



Lumsdon & Evans, *J. Coll. Interf. Sci.* **164**, 119 (1993)

Colloid Behavior of Goethite Nanoparticles

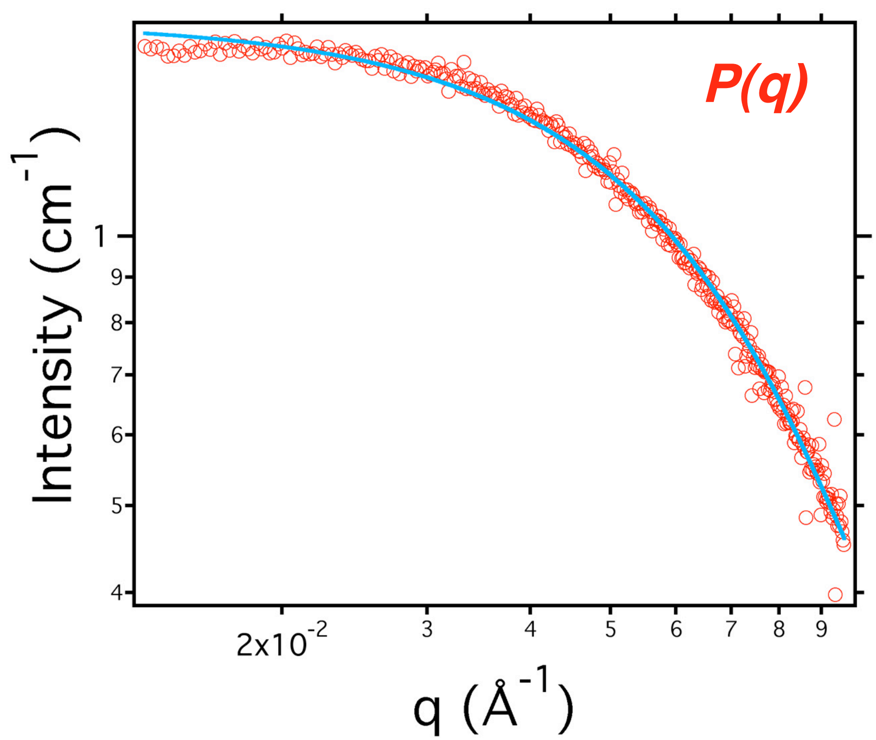
SAXS of 6 nm diameter FeOOH nanoparticles at **pH 5.0** vs. ionic strength

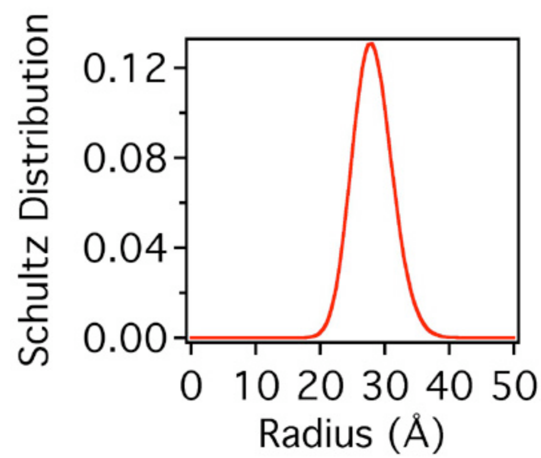


Colloid Behavior of Goethite Nanoparticles

Single particle scattering at **pH 5.0** and 10^{-3} M $NaNO_3$

Fit particle size and size distribution

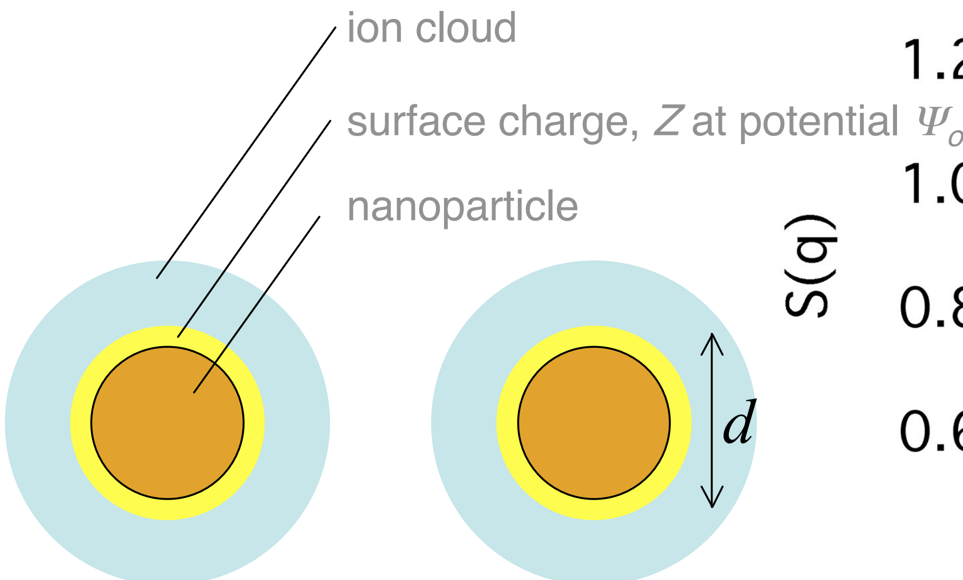




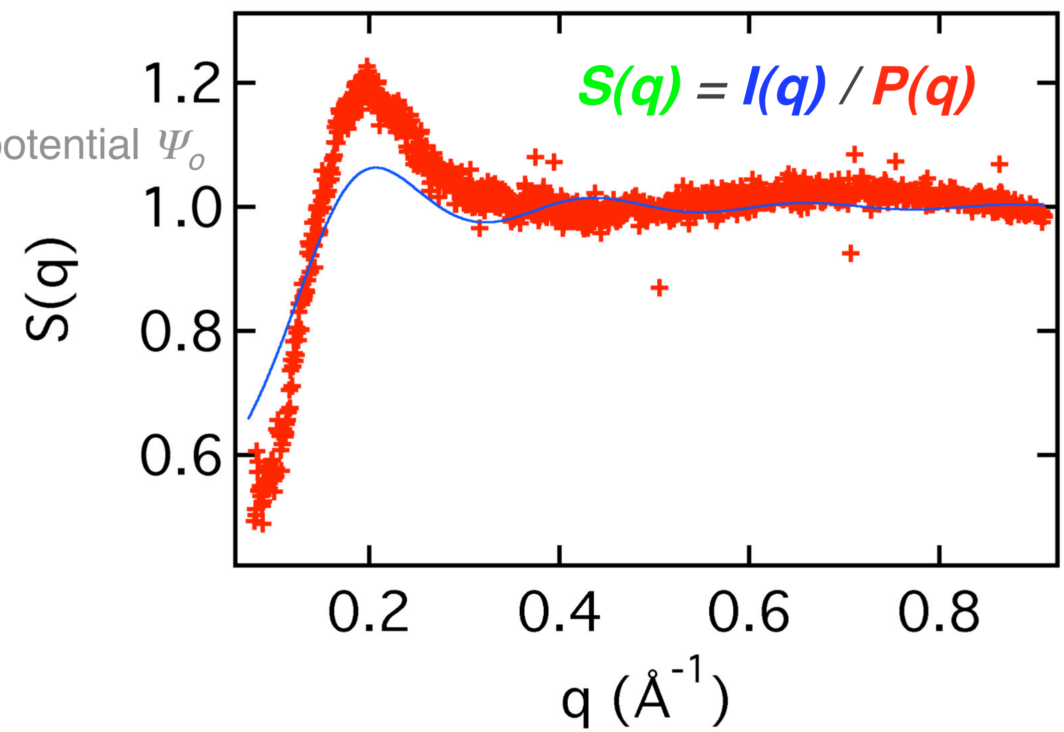
Colloid Behavior of Goethite Nanoparticles

Structure factor at **pH 5.0** and 10^{-4} M $NaNO_3$

Fit electrostatic parameters, Z^{eff}, κ^{eff}.



$$V(r) \approx \frac{\varepsilon \varepsilon d^2 \psi_o}{r} \exp\left[-\kappa(r-d)\right]$$



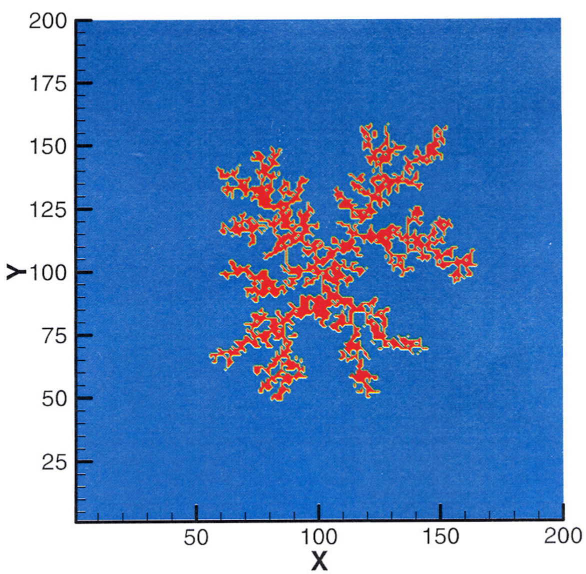
Simulating the Structure of Goethite Nanoparticle Aggregates

Lattice Boltzmann:

Currently limited to 2D!

growth of fractal crystal structures

simulated SAXS patterns

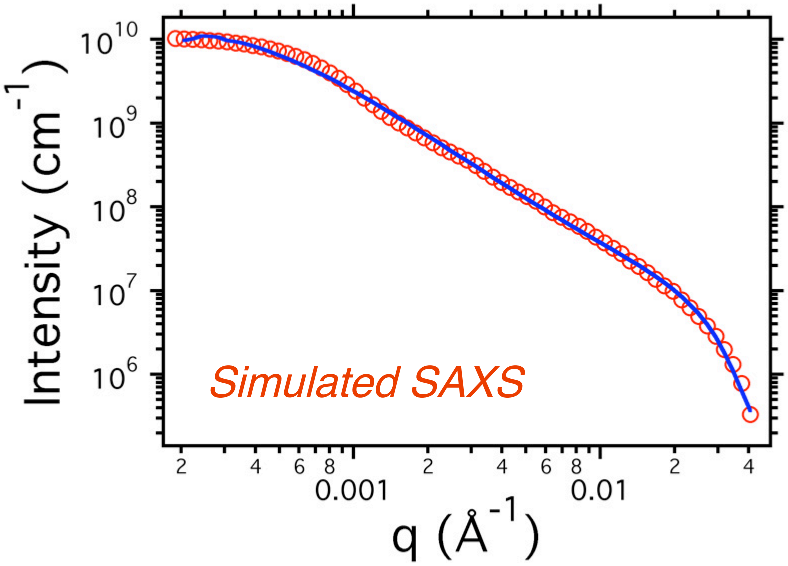


LB Simulation by Guopeng Lu

Fit to simulated data:

D_F = 1.6

Cluster radius ~ 50 Å



LB Theory: Kang et al., *Geophys. Res. Lett.* **31**, L21604 (2004)

SAXS from Fractal Aggregates

Two length scales

individual particle size, r_o

largest cluster size, ξ

$$\left[g(r)-1\right] \propto \frac{r^{D_F-3}}{r_o^{D_F}} \exp(-r/\xi)$$

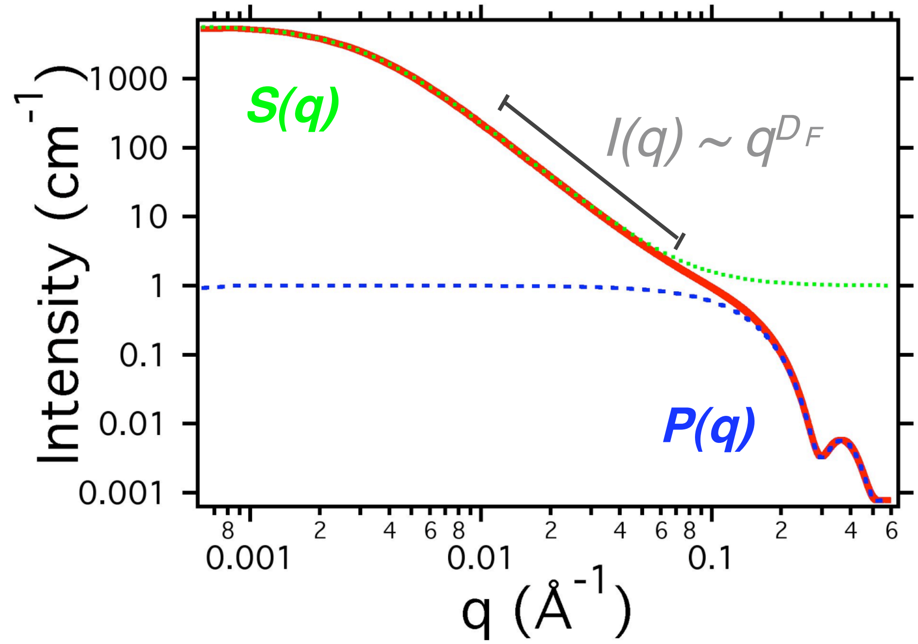
Fractal dimension, D_F

Efficiency of space filling

SAXS can measure size & D_F

ANALYTICAL APPROACH

$I(q) \sim S(q)P(q)$

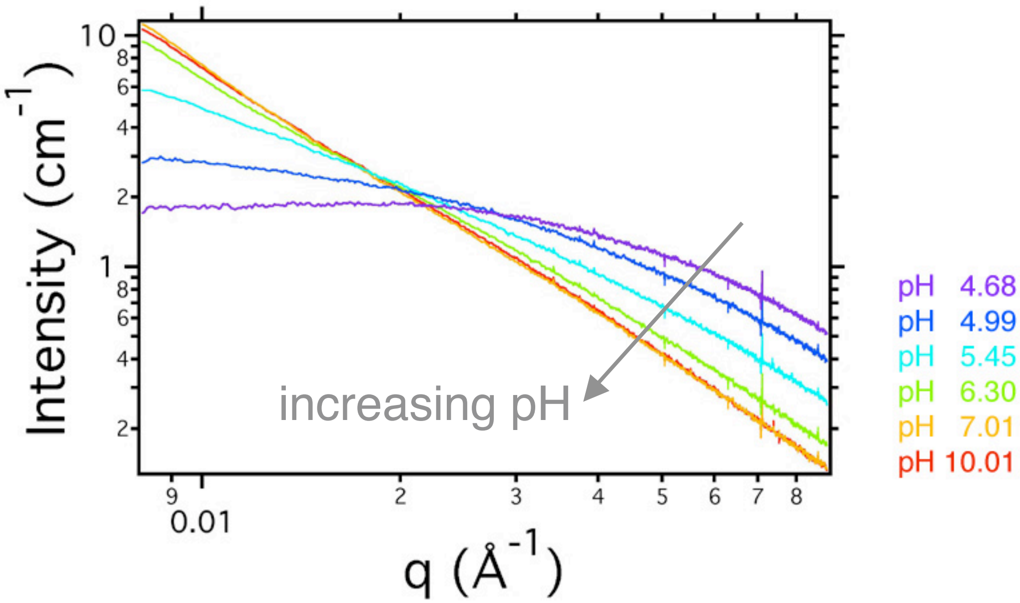


$d = \dfrac{2\pi}{q}$

Teixeira, *J. Appl. Cryst.* **21**, 781 (1988)

Colloid Behavior of Goethite Nanoparticles

SAXS of 6 nm diameter FeOOH nanoparticles vs. pH
Volume Fraction = 0.075 %; 10^{-2} M $NaNO_3$



Colloid Behavior of Goethite Nanoparticles

SAXS of 6 nm diameter FeOOH nanoparticles vs. pH
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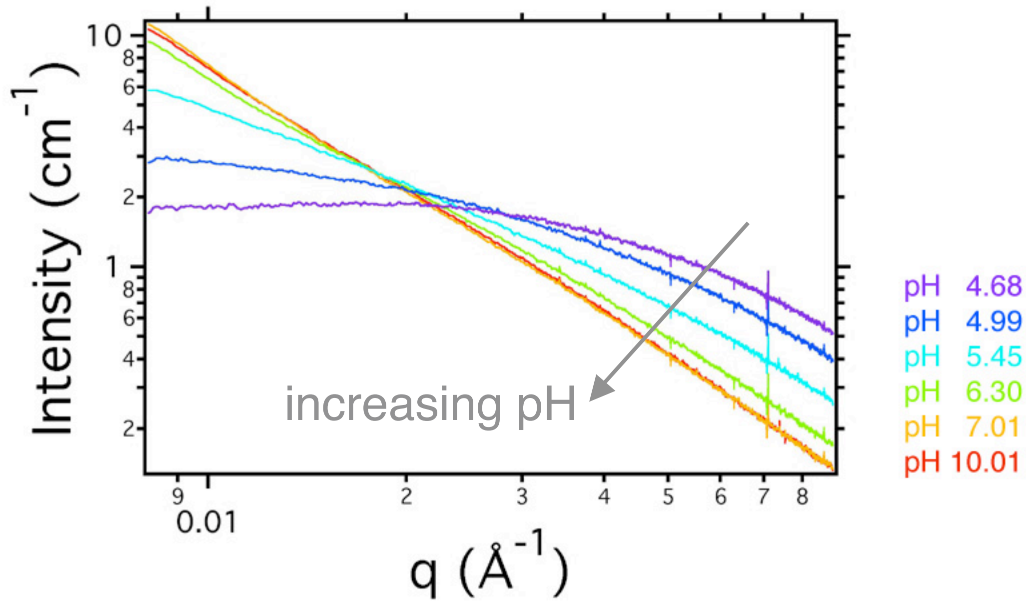
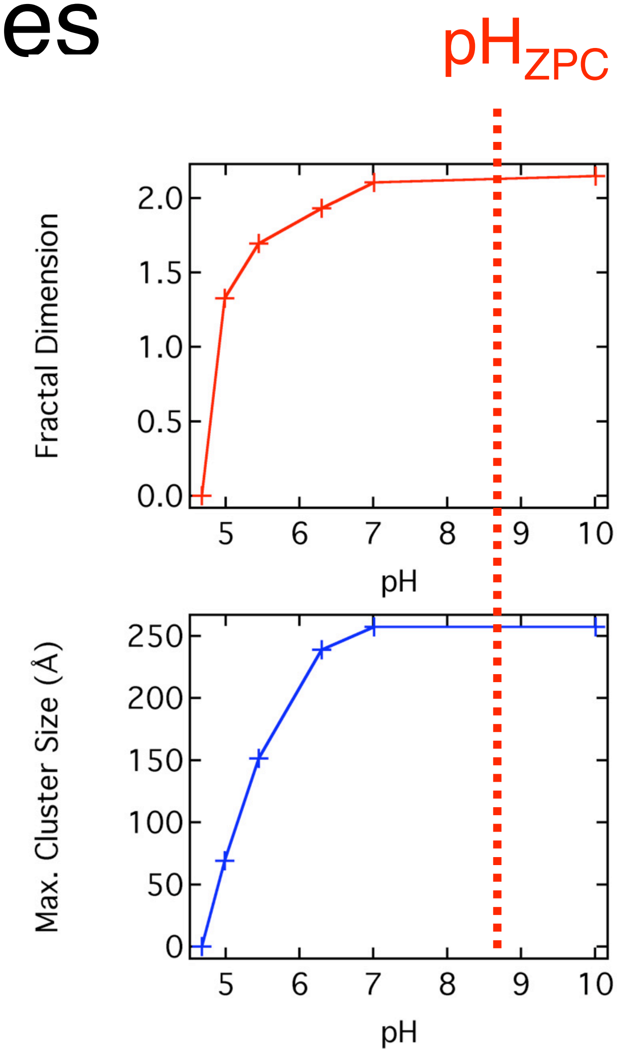
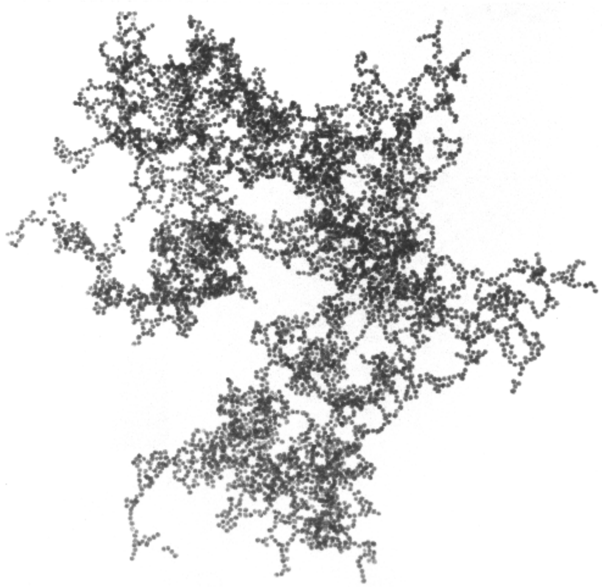




SAXS from Fractal Aggregates

Numerical simulation

Reveals breakdown of fractal description at low *r*



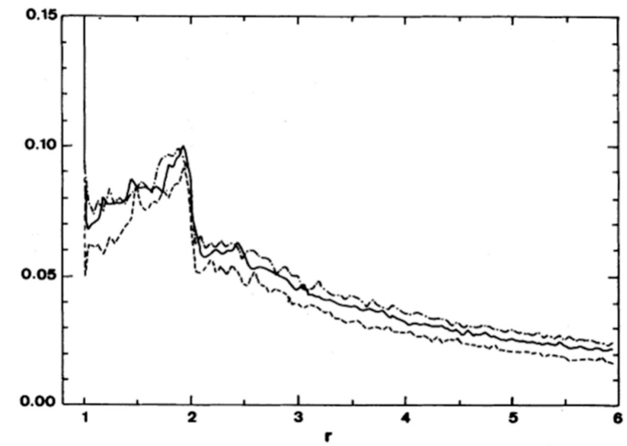
Fractal properties not well-defined for < 50 particles

Lattuada et al., *J. Coll. Interf. Sci.* **268**, 106 (2003)

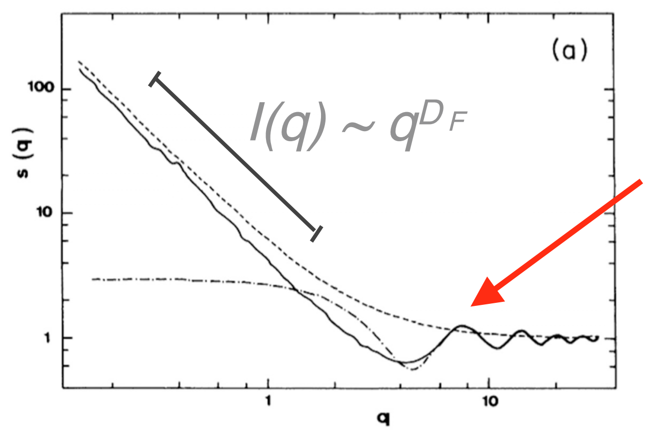
Monodisperse particles

Sharp peaks in *g(r)* and *S(q)*

g(r)



S(q)



Hasmy et al., *Phys. Rev. B* **48**, 9345 (1993)

Conclusions

- Coulombic repulsion evident in non-aggregated suspensions of goethite nanoparticles.
  - Larger data set and better analysis required to parameterize effective pair potentials

- Nanoparticles form aggregated clusters with fractal internal structure well below the pH_{zpc}
  - Morphology & short-range structure uncertain

- Cluster size and density dependent on solution condition, as expected
  - What determines maximum cluster size?

Simulating the Structure of Goethite Nanoparticle Aggregates

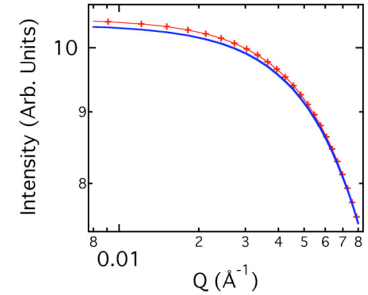
Long term goal:

Lattice Boltzmann simulations
- interparticle interaction forces
- hydrodynamic behavior

Alternative:

Simulated annealing
- no physical description
- seek agreement with SAXS data

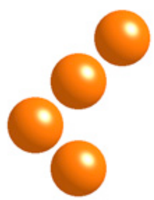
Simulating the Structure of Goethite Nanoparticle Aggregates

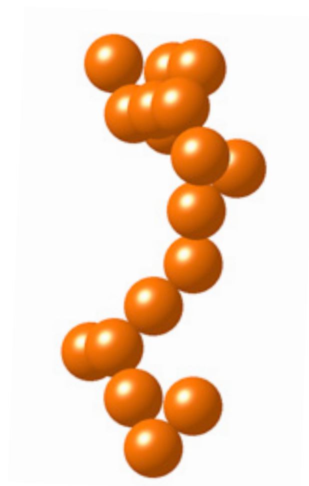


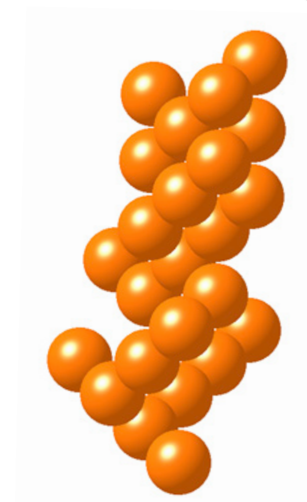
Simulated annealing:

DAMMIN code optimized for macromolecules

porous structures possible in principle







pH 4.99 | pH 5.45 | pH 6.30

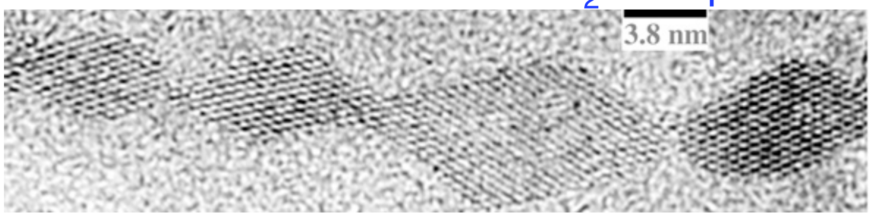
Svergun, *Biophysical J.* **76**, 2879 (1999)

Simulating the Structure of Goethite Nanoparticle Aggregates

Linear aggregates?

TEM observations and **MD** simulation highlight role of *anisotropic structure*

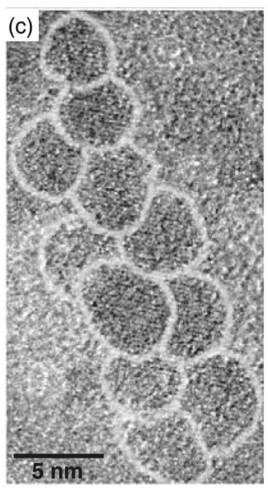
TiO_2 nanoparticles



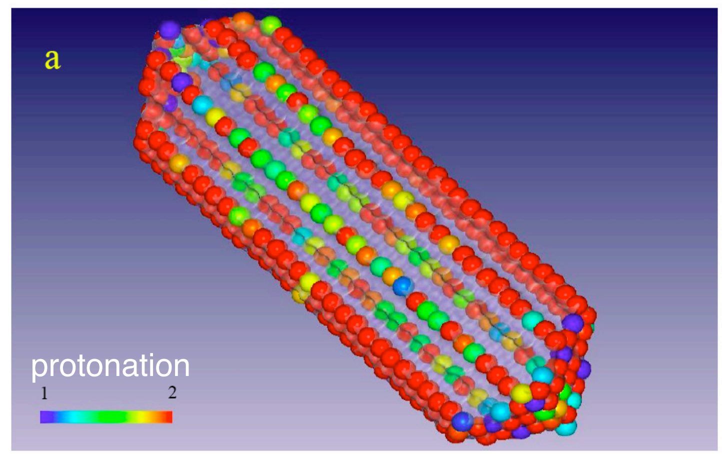
Penn & Banfield *Am. Mineral.* **83**, 1077 (1998)

FeOOH nanoparticles

Guyodo et al., *Geophys. Res. Lett.* **30**, 1512 (2003)



Rustad & Felmy *Geochim. Cosmochim. Acta*, **69**, 1405 (2005)

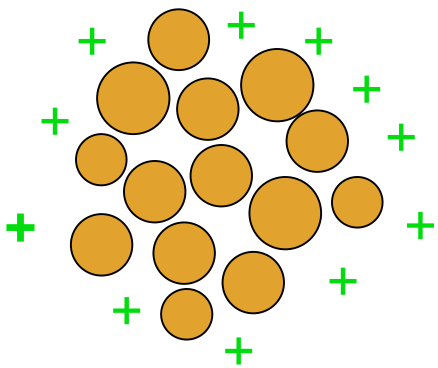


Simulating the Structure of Goethite Nanoparticle Aggregates

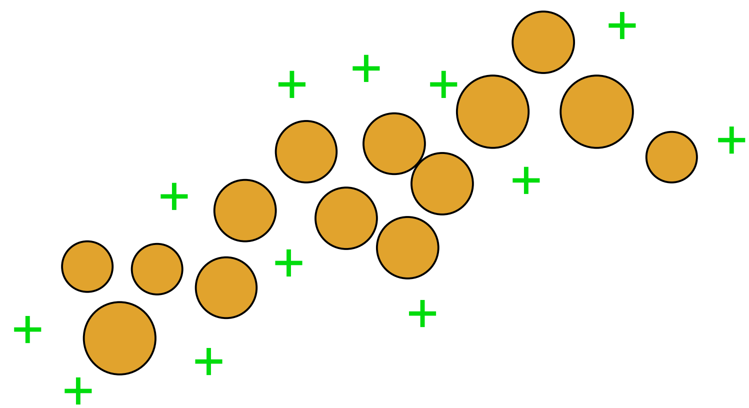
Linear aggregates?

Monte Carlo simulations (2D) highlight role of *repulsive interactions*

High energy aggregate



Low energy aggregate



Lebovka et al., *EuroPhys. Lett*. **41**, 19 (1998)

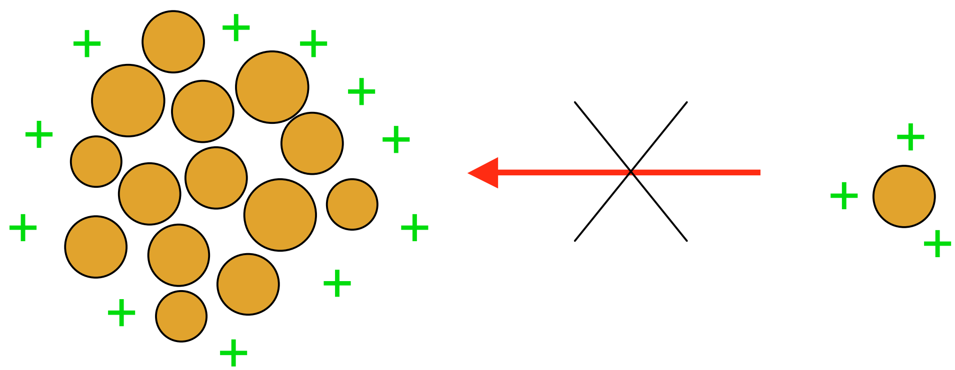
Simulating the Structure of Goethite Nanoparticle Aggregates

Repulsive interactions likely limit maximum cluster size

Particle-cluster and cluster-cluster aggregation halts when:

$$z\Psi > kT$$

pH dependent!



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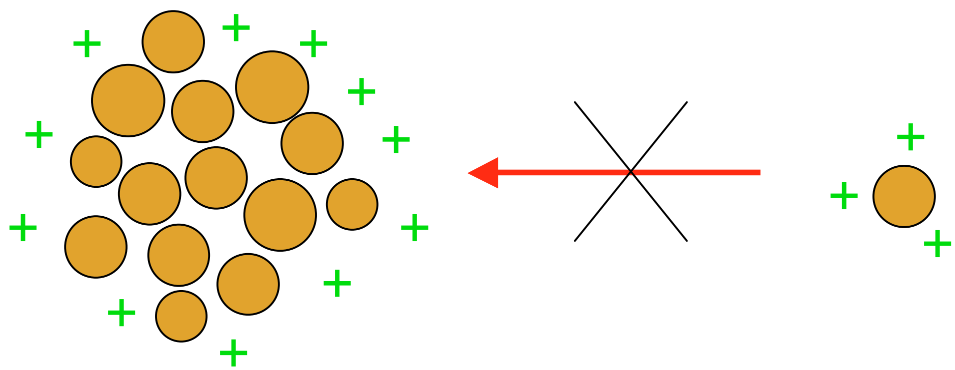
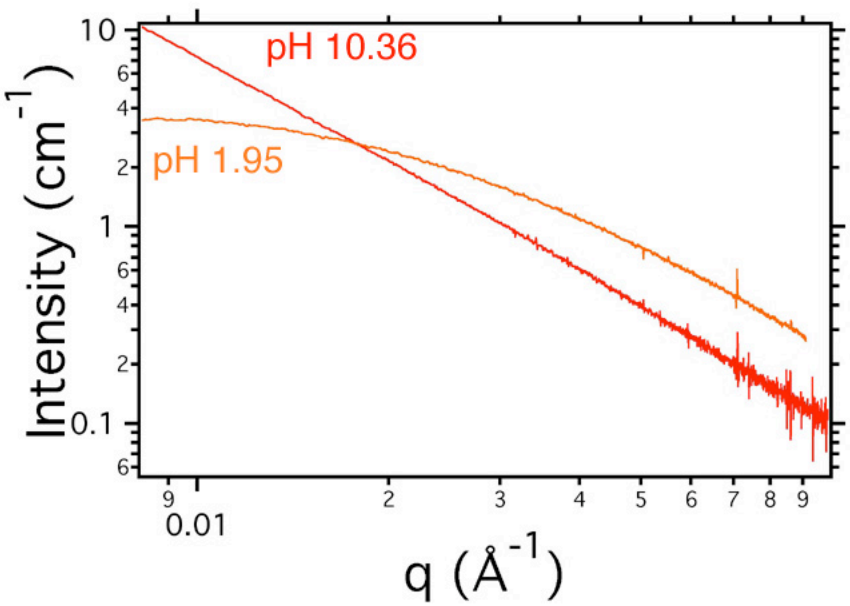
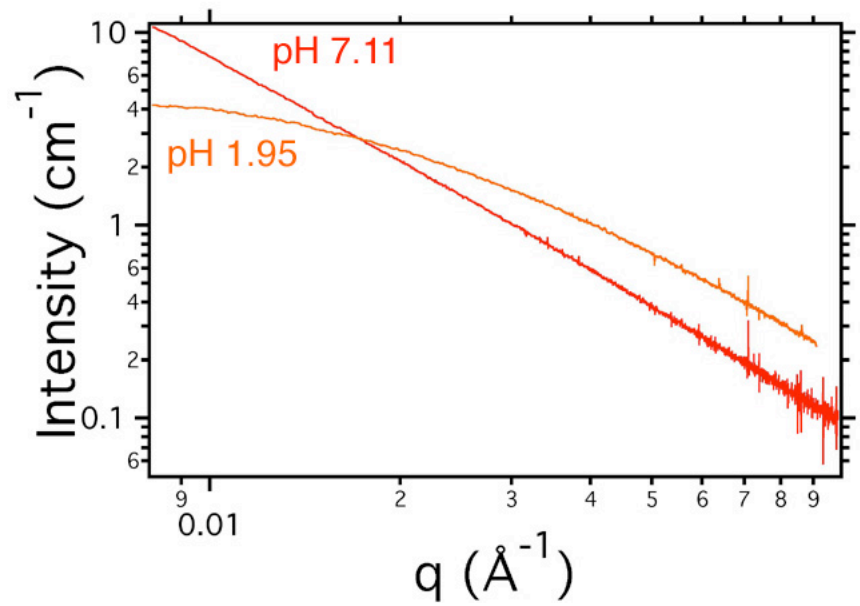


Partial Disaggregation of Goethite Clusters

Almost reversible process …





Partial Disaggregation of Goethite Clusters

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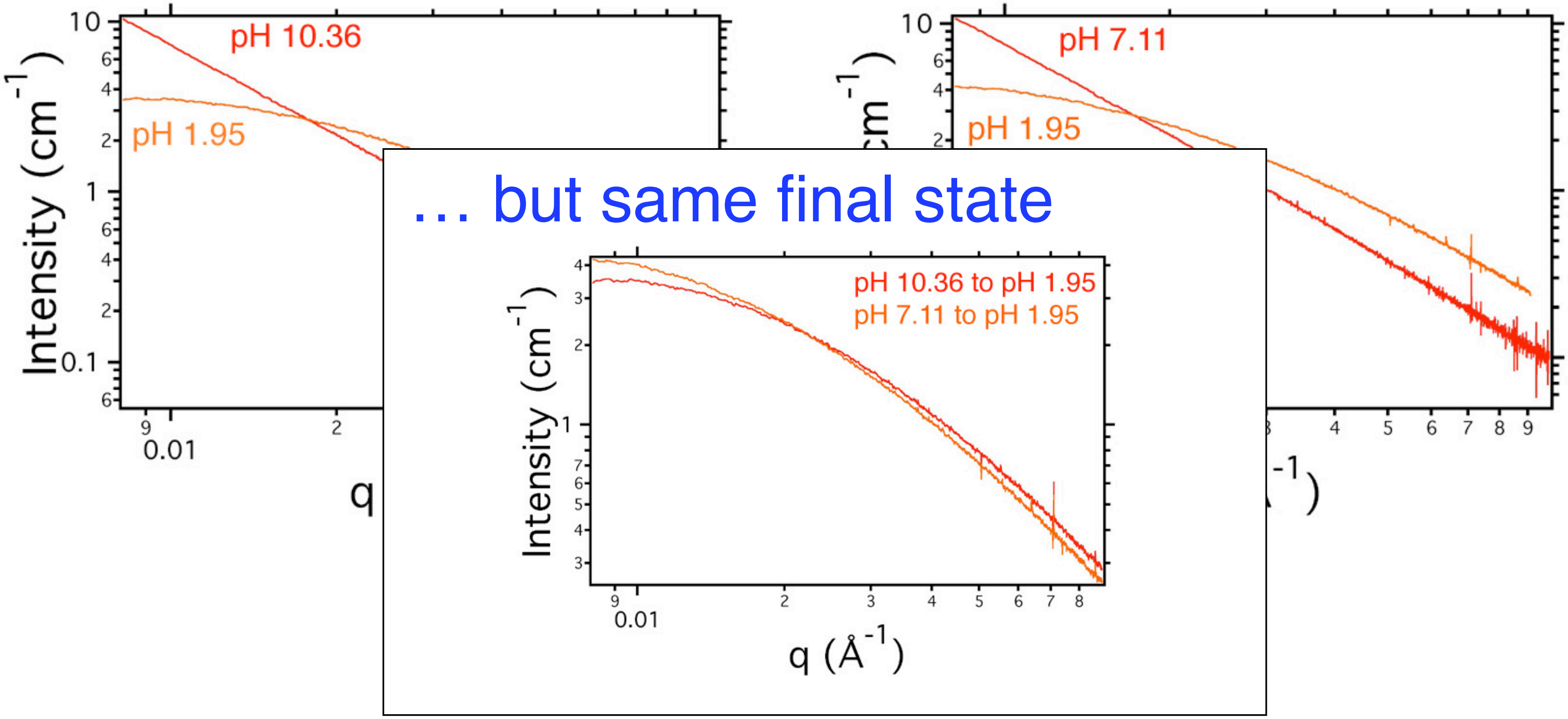
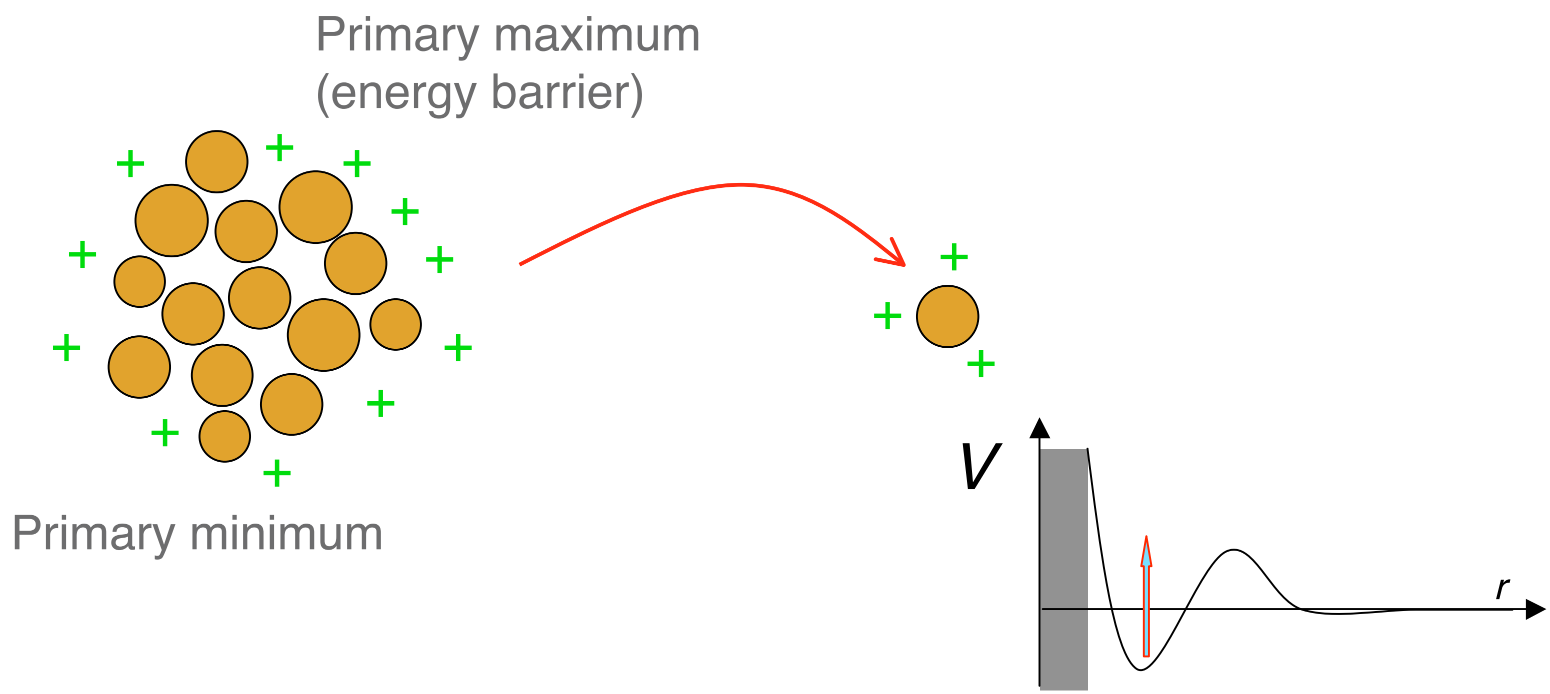


Partial Disaggregation of Goethite Clusters

Surface charge drive partial disaggregation?

- Finite potential well upon aggregation
- Test short-range interaction potentials in simulation



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